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# HETEROGENEITY OF SURFACES

## Immersion Calorimetry and Adsorption Studies
## of
## The Heterogeneous Nature of Nickel and Carbon Surfaces

*Project Supervisor* · · · · A. C. ZETTLEMOYER

*Investigators* · J. J. CHESSICK, F. H. HEALEY, Y. YU

The Surface Chemistry Laboratory
Lehigh University
Bethlehem, Penna.

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# ABSTRACT

I.        Isotherms for the adsorption of argon on oxide-coated nickel powder and on this sample after each of several reductions with dry hydrogen at 350° were determined at -195° and -183°.  Equilibrium functions, isosteric heats of adsorption and integral molar entropy values were calculated.  These data showed a marked difference in the surface nature of the unreduced and reduced samples.  However, the adsorption behavior of argon on the reduced samples was similar above monolayer coverage.  In this region of adsorption the only effect of reductions at high temperature was to cause an increase in particle size due to sintering without markedly changing the surface nature of the reduced metal powder.

The equilibrium function and isosteric heat data indicated that both the unreduced and reduced samples were heterogeneous.  Adsorption sites of higher energy as well as a wider distribution of sites characterized the unreduced samples. Stronger cooperative effects leading to an increase in heat values and a subsequent maximum near monolayer coverage was found for argon adsorption on the reduced sample.

On the basis of experimental and calculated integral entropy values, a model of localized adsorption on a heterogeneous surface without adsorbate interactions explains the adsorption of argon on the unreduced and reduced sample.  This model is probably not valid beyond $\theta = 0.5$ for the unreduced sample and beyond the relatively low value of $\theta = 0.2$ for the reduced sample; above these $\theta$ values lateral interaction set in.  At very low coverages on both samples the heterogeneous nature of the surfaces was evident from the low molar entropy values $S_S$ and small configurational entropy contributions.


II.        A low temperature calorimeter to measure heats of immersional wetting in liquid nitrogen, has been constructed. The heats of immersion of magnesia, silene, alumina and Graphon (a graphitized carbon black) in liquid nitrogen were found to be practically the same.  Thus, a simple determination of the heat evolved in terms of the volume of liquid nitrogen vaporized when the clean solid is broken under the liquid may be used to measure specific area.

Theoretical values for the heat of immersion of magnesia in liquid nitrogen have been calculated by two methods from adsorption data, and were found to compare favorably with the experimental value.  The contribution of the free energy term to the heat of immersion was approximately one-third that of the $T\Delta S$ contribution.

III.   The effect of increasing the amount of surface oxide on Graphon on both the water vapor adsorption isotherms and the heat of immersion in water was studied. Oxidations were carried out at $530^C$ with both dynamic and static oxygen atmospheres for successive periods up to 20 hours total. While the volume of water adsorbed increased regularly with the time of oxidation, the shape of the isotherm up to a relative pressure of 0.6 remained unchanged; plots of surface coverage vs. relative pressure were identical for the original sample and for the various oxidized samples.

The weight loss due to formation of volatile oxides of carbon was a linear function of time of oxidation whereas the formation of surface oxide appeared to follow a parabolic rate curve. The ratio of the apparent area available to water adsorption to the total area of Graphon determined by nitrogen adsorption was taken as a measure of the fraction of surface oxidized. After activation for two hours at $900^O$ the sample showed a considerable decrease in the number of hydrophilic sites due to volatilization of oxygen complexes on the surface of the original sample.

The heat of immersion in water did not prove to be a linear function of the fraction of hydrophilic surface. The increasing slope of the heat of immersion vs. hydrophilic fraction appeared to indicate that interactions between molecules adsorbed on adjacent patches of oxide sites increased as the number of patches on the surface increased. The slope and intercept of the curve for the more hydrophobic samples was used to estimate the heat of wetting of the carbon surface and of the hydrophilic sites.

## GENERAL INTRODUCTION

The investigation of surface heterogeneity in this laboratory has demonstrated that a metallic surface may have both a real physical heterogeneity due to surface irregularities and an apparent chemical heterogeneity due to changes in the work function of the metal during the adsorption process. In addition, heterogeneities of particular importance in chemisorption result from the presence of chemical impurities on the surface of the adsorbent. These three types were shown (Technical Report No. 4) to be important to an understanding of the behavior of molybdenum towards oxygen at low temperatures.

The studies of Graphon (Technical Report No. 5) by gas adsorption and also by a newly developed immersional calorimetric technique illustrated the role of active sites in the adsorption process even though they are only sparsely distributed on the surface. Without the development of the immersion calorimeter, the thermodynamic data necessary for the elucidation of the mechanism of water adsorption on Graphon would have been impossible. Furthermore, the combination of adsorption and calorimetric measurements greatly widens the range of solid systems that can be studied. Thus, a previous study of the oxide films on nickel, steel, and molybdenum (Technical Report No. 5) illustrated the value of heat of immersion data in obtaining a quantitative measure of the porosity and hydrous nature of oxide coatings. For asbestos,

the linearity of the heat of immersion curve with increasing amount of water preadsorbed provided elegant confirmation of the surface homogeneity of this material.

The role of surface heterogeneities such as crystal edges, cracks, lattice defects, and grain boundaries in chemisorption is highly controversial. Wheeler (1) points out that

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(1) Structure and Properties of Solid Surfaces, Univ. of Chicago Press, Chicago, Illinois (1953) p. 458.

---

the possibilities of the properties of plane crystal surfaces and their role in chemisorption should be exhausted before heterogeneities should be invoked. Furthermore, a new concept of the process of chemisorption has been advanced by workers (2)(3) who seek the explanation for chemisorption in terms of

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(2) M. Boudart, J. Am. Chem. Soc. 74, 1531 (1952).

(3) D.H. Dowden, J. Chem. Soc., p. 242 (1950).

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the band theory of metals, or more explicitly in terms of the changes in the Fermi level of the metal and the distribution and occupancy of the electron energy levels at the Fermi surface as chemisorption proceeds. Boudart's model accounts for the main facts of chemisorption without directly involving the presence of the usual types of surface heterogeneities although there exists

a marked similarity between this picture and that of "apparent"
chemical heterogeneity defined in our Technical Report No. 5.
Dowden's views are most complete since they include the effect
of chemical and physical heterogeneities. In addition,
Volkenshtein (4) has introduced the interesting idea that

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(4)  F. F. Volkenshtein, Zh. Fiz. Khimu. 23, 917 (1949).

---

heterogeneities are mobile and can interact. To assess the
value of these new ideas a critical survey of the current data
and theories of the role of surface heterogeneities in chemi-
sorption was undertaken (presented at the Gordon Conferences
on Corrosion and on Chemistry at Interfaces). A summary of this
study will form the basis for a future technical report in this
series. It may be categorically stated, however, that certain
chemisorption results from this Laboratory, as well as data
presented in the recent literature, could not be explained at
present without recourse to the heterogeneity concept.

The present report contains three sections covering
various phases of the project in manuscript form:

1. The results of a study of the heterogeneous
nature of oxide-coated and reduced nickel samples by the adsorp-
tion of argon at low temperature.

2. A description of a newly designed and constructed
immersion calorimeter used to obtain heats of wetting of solids

in liquid nitrogen and its application to a study of a sample of magnesia which had been extensively studied by adsorption methods.

3. A study of the system water-Graphon and the heterogeneities introduced by successive oxidations at high temperature.

A summary of work in progress is also included.

ADSORPTION STUDIES ON METALS IV.
THE PHYSICAL ADSORPTION OF ARGON ON
OXIDE-COATED AND REDUCED NICKEL

## INTRODUCTION

Gas adsorption techniques were employed in this laboratory to study the surface heterogeniety of molybdenum metal (1). A thick oxide film was formed on the molybdenum

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(1) F.H. Healey, J.J. Chessick and A.C. Zettlemoyer, J. Phys. Chem. 57, 178 (1953).

_____

surface after exposure to moist air during storage. Reduction of this polymolecular oxide film by high temperature treatment with dry hydrogen increased the surface roughness or physical surface heterogeniety. After successive heatings in the presence of hydrogen a lower limit of surface area was reached. For a further understanding of metallic surface properties, this work has been extended to nickel.

Through the development of adsorption thermodynamics and its application to various adsorption systems in the last decade, it is now well established that thermodynamic functions are very useful for characterizing the properties of adsorbed films. However, since the complexity of the different existing forces and the wide differences in surfaces, it is helpful to investigate more than one function before reaching final conclusions. A sharp initial drop of the isosteric heat with increasing

surface coverage is generally attributed to the surface hetero-
geniety.   Following Hill's (2) statistical development, the

(2)   T.L. Hill, J. Chem. Phys. 17, 262 (1949).

entropy of the adsorbed phase could be evaluated, which serves
as a parameter for defining a surface.   Furthermore, Morrison
and Drain (3) were able to calculate the configurational and

(3)   J.M. Drain, J.A. Morrison, Trans. Faraday Soc. 48, 316 (1952).

non-configurational entropy values of system consisting of a
heterogeneous surface.   Recently, Graham (4) has introduced

(4)   D. Graham, J. Phys. Chem. 57, 665 (1953).

the equilibrium constant of a localized adsorption system for
characterizing a surface.   Very little work has been done with
the last method.   In the present work the conclusions from this
free energy function are compared to those of isosteric heats
and entropies.

# EXPERIMENTAL

Materials and Apparatus - The nickel sample furnished by the International Nickel Company had a reported purity when first prepared greater than 99%, and a particle size range from 2 to 25 microns. The sample was passed through a 400 mesh sieve before use to remove large particles.

High purity tank argon and helium were used. The argon was further purified by passage through fine copper gauze heated to 500° and dried with magnesium perchlorate. Helium was purified by passage through a charcoal trap immersed in liquid nitrogen.

Tank hydrogen, 99.8% pure, was passed slowly through a Baker Deoxo Unit, containing a palladium catalyst, and then through a drying train consisting of two magnesium perchlorate driers, a phosphorous pentaoxide tube and a cold trap immersed in liquid nitrogen. Previous work in this laboratory showed that water diffused into the reduction system if rubber connections were used. Therefore, the reduction system was of all-glass construction with Tygon tubing connections.

An Orr type (5) apparatus was used. Apiezon B oil which

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(5)  W. J. C. Orr, Proc. Roy. Soc. (London), 173A, 349 (1939).

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had a very low vapor pressure and did not dissolve measurable amounts of the gases studied was used in the manometers. Pressures as low as 0.005 cm. Hg. were measured with this oil. However, the height of the manometer restricted pressure measurements to about

5 cm. Hg. To increase the range of the manometer, a back pressure was applied to the vacuum side of the manometer for pressures greater than 5 cm. Hg. In this way, adsorption pressures as high as 20 cm. Hg. were obtained.

It was shown previously (6) that samples with an area

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(6) J.J. Chessick, Ph. D. Thesis, Lehigh University (1952).

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as low as 0.5 m$^2$ could be studied with precision with this apparatus. Nevertheless, in this investigation sufficiently large samples were taken so that the total area ranged from 3 to 7 cm$^2$.

Pretreatment of Samples - The unreduced, polycrystalline samples were first washed with absolute alcohol to remove any organic film. They were then degassed at room temperature for at least 12 hours to an ultimate pressure below 10$^{-5}$mm. Hg. before adsorption measurements were made.

Reduction of the surface oxide which had formed on the nickel powders on exposure to moist air during storage (1), were carried out at 350$^C$. The hydrogen after thorough drying was passed slowly through the samples at atmospheric pressure. The reduction times are listed in Table 1. Two nickel samples which differed slightly in area but were obtained from the same batch were studied. The first sample was subjected to four reductions. After each reduction the sample was degassed at 25$^{\circ}$ to 10$^{-5}$mm. Hg. for 6 hours, then argon adsorption isotherms were determined at -195$^{\circ}$. The second sample was studied primarily to substantiate

the results found with the first sample as well as to obtain some additional data for the adsorption of argon at -183° and -195°. After the desired adsorption measurements were made, the samples was again subjected to hydrogen treatment at 350°. Since the reduced nickel was never exposed to any gas except non-reactive helium and argon after the first reduction, the second and sub-sequent hydrogen treatments were not strictly reductions. Rather they were conducted to allow a study of the change of the surface properties of the metal as sintering progressed; they are labeled reductions merely as a convenience. The hydrogen was used to provide for any accidental contamination of the metal by air during the course of the adsorption measurements.

No effort was made to remove sorbed hydrogen from the reduced samples by degassing at elevated temperatures, since the primary objective of this investigation was to characterize two different surfaces - the oxide-coated and that produced by reduction-by gas adsorption methods. However, to determine the effect of this sorbed hydrogen on the reduced samples on the adsorption of argon, a separate sample was reduced under the usual conditions and degassed at 350° for 3 hours. Large amounts of hydrogen were evolved. Isotherms reduced to unit surface area for this sample and other samples which were reduced but not degassed at high temperature were found to coincide exactly above monolayer coverage indicating that in this region the argon adsorption was independent of any hydrogen presorbed. Beeck (7) also found that the adsorption

(7)  O. Beeck, Advances in Catalysis, Acedemic Press, N.Y.C.
     Vol. II (1950) p. 160.

of krypton on nickel films was independent of hydrogen pre-
sorbed in his sample.

Procedure - One of the often unrecognized difficulties
in adsorption studies at low temperatures is the slow attainment
of equilibrium at small adsorption pressures. Spurious rates or
heat curves have been shown to result when insufficient time
has been allowed for equilibrium (6)(8). To accelerate thermal

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(8)   F. C. Tompkin, Trans. Faraday Soc., 34, 1469 (1938).

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equilibrium in the low pressure region, it was found expedient
to precool the sample in the presence of helium at the adsorp-
tion temperature for 2 or 3 hours before adsorption measurements
were made. The system was then degassed for 30 minutes at the
adsorption temperature and argon adsorption measurements begun.
As a result of precooling, equilibrium at pressures below 0.1 mm.
was attained within 15 minutes. At high pressures adsorption
was complete within 5 minutes.

# RESULTS AND DISCUSSION

Adsorption Isotherms - Argon adsorption isotherms measured at -195° on unreduced, oxide-coated nickel and on this sample after each of four successive reductions at 350° are shown plotted in Figure 1. The shapes of the isotherms indicated a marked difference in the behavior of argon adsorbed on the unreduced and reduced powders. Contrariwise, isotherms for argon adsorbed on the reduced nickel samples were found to be very nearly parallel in the region above monolayer coverage although they showed a decrease in the amount adsorbed after each reduction. This decrease, which exponentially approached a limiting value, resulted from a definite increase in particle size of the metal powder due to sintering at the reduction temperature. Confirmation of these initial results was obtained when similar studies were conducted on a new sample of lower initial area but obtained from the same batch of nickel powder. Furthermore, the temperature dependency for adsorption on this second sample was determined at -183° and 195° and isosteric heats of adsorption were calculated.

Some tentative conclusions concerning the natures of the nickel surfaces before and after reduction were possible from a knowledge of the prehistory of the nickel and a visual inspection of these isotherms. First, since the metal was polycrystalline, it was reasonable to assume that the surfaces were heterogeneous. Further, it was concluded that the distributions

FIGURE I

UNREDUCED

REDUCTION   I
     "      II
     "      III
     "      IV

VOLUME ADSORBED  MLS.TP/GM.

RELATIVE PRESSURE  P/P₀
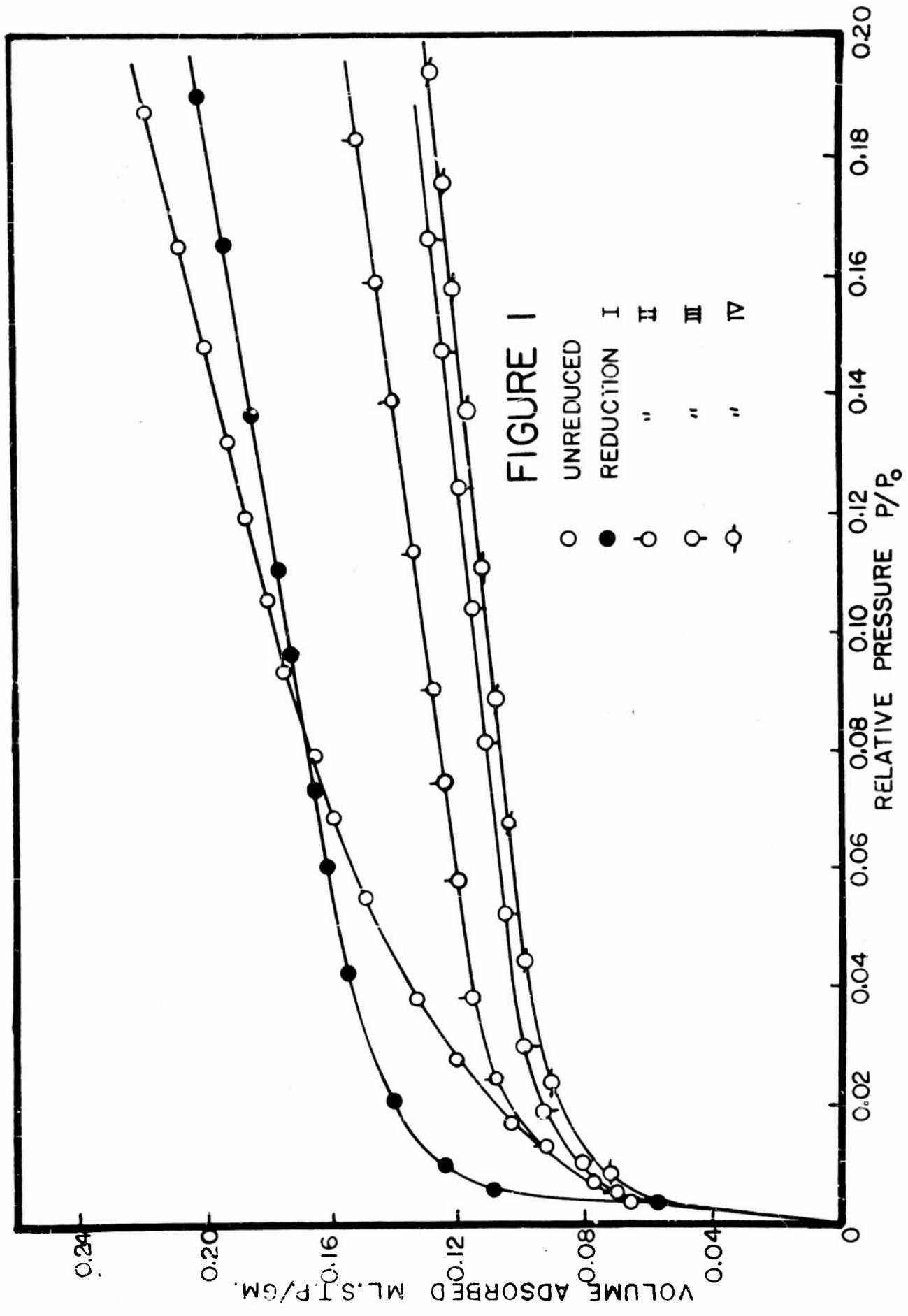
of adsorption energy sites on the oxide-coated and reduced metal were quite different. Finally, it appeared that while a new type of surface resulted after reduction of the oxide film, the effect on this new surface of sintering at high temperature was to cause a decrease in area without drastically changing its site energy distribution, particularly at higher coverages. Considerable evidence was obtained to substantiate these findings as well as to yield more quantitative information on the nature of these two different surfaces.

Adsorption Isotherms Reduced to Unit Surface Area - Adsorption in the first layer, whether chemical or physical, depends on two factors:  the extent of the surface and the energy of interaction between surface and adsorbate. Brunauer (9)

(9)  S. Brunauer, The Adsorption of Gases and Vapors, Princeton Univ. Press, Princeton, N.J. (1943) p. 329.

designated the former the "non-specific" factor, the latter the "specific" factor in adsorption. This delineation was, of course, an oversimplification since the interactions between adjacent adsorbed molecules can be an important additional factor. However, if physical adsorption were completely "non-specific", then surface area alone would be controlling and isotherms for a gas adsorbed on all types of surfaces would coincide if volumes adsorbed per unit area were plotted against pressure. This situation would not exist, on the other hand, if surface "specificities" were also important. Isotherms of this nature were developed in order to differentiate between the adsorption behavior of argon on both

the unreduced and reduced nickel samples. For this reason a meas-
ure of the specific areas of these samples was necessary.

The values for $V_m$ were obtained by the usual BET
method and represented the STP volumes of gas required to cover
the surface of one gram of sample with one adsorbed layer. The
specific areas of the samples were calculated from these $V_m$
values assuming that the adsorbed molecules have the same hexagonal,
close-packing as in the liquid state (10). Another method, the

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(10) ibid, p. 287.

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"B" point method of obtaining $V_m$ and corresponding area values,
was to use the volume adsorbed at the beginning of the linear
portion of the Type II isotherms. This latter method was adopted
here because of the better agreement in area values calculated
from $V_m$ values at $-183^\circ$ and $-195^\circ$ obtained by this "B" point
method. This agreement is shown in the last column of Table I
for sample No. 2.

The isotherms measured for the adsorption of argon on
unreduced nickel and on this same sample after each of four,
successive, high temperature reductions are shown in Figure 2.
The adsorption values were reduced to unit area; i.e., $V/V_m$ values
were plotted against relative pressure. There was no doubt that
the "specific" forces whether surface, adsorbate interaction or
both were different for argon adsorbed on unreduced and reduced
nickel. On the other hand, the coincidence of the four isotherms
for the reduced samples, although they differed in area by as much

FIGURE 2

| UNREDUCED | REDUCTION | I | II | III | IV |
|-----------|-----------|---|----|----|----|

SURFACE COVERAGE $\theta$

RELATIVE PRESSURE $P/P_0$
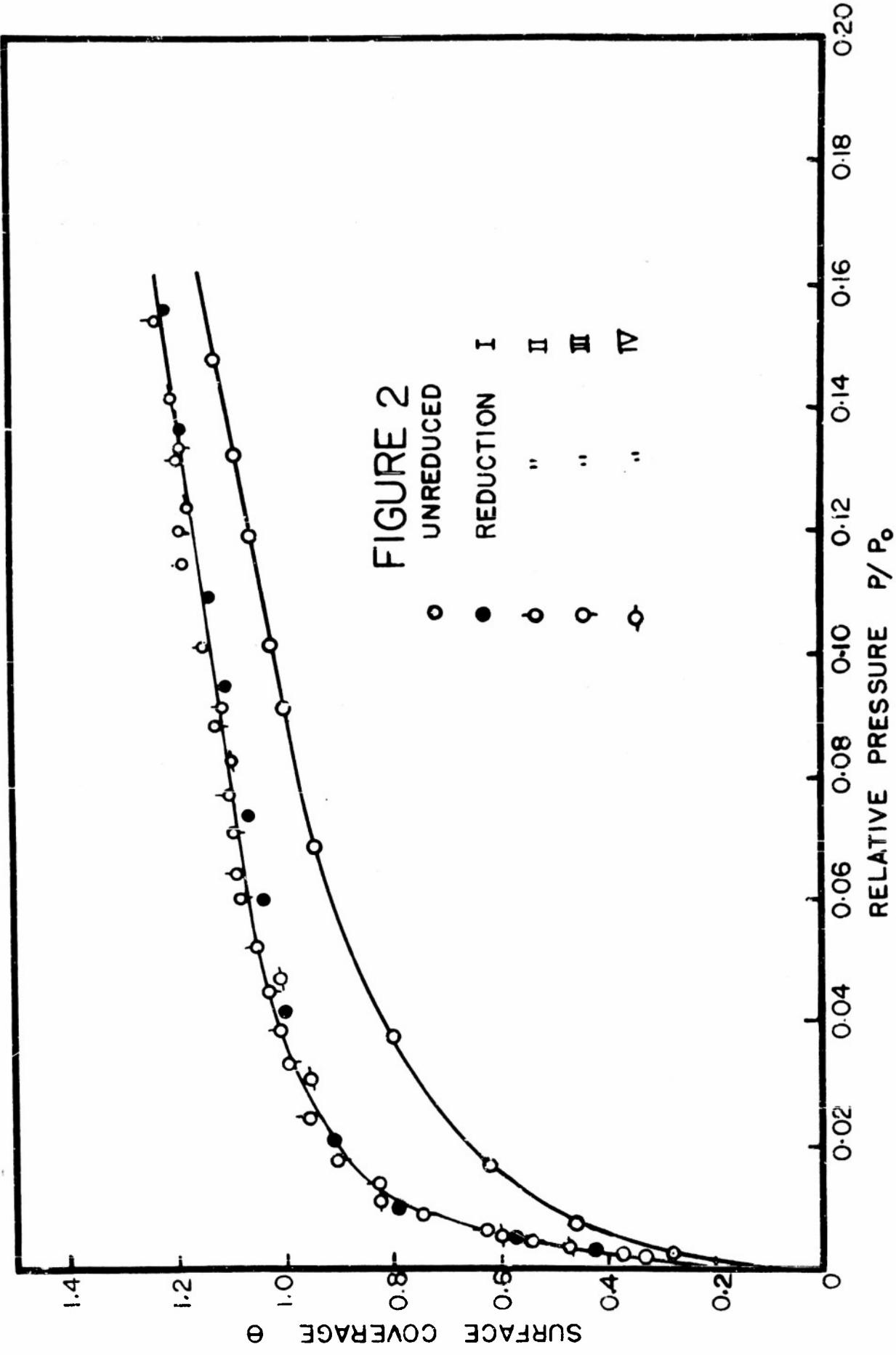
## TABLE I

### ADSORPTION OF ARGON ON NICKEL

| Reduction No. | Time (hrs.) | BET | | "B" Point | |
|---|---|---|---|---|---|
| | | $V_m$ (ml./g.) | Area $(m^2/g.)$ | $V_m$ (ml./g.) | Area $(m^2/g.)$ |
| Sample #1 $-195^{\circ}C.$ | | | | | |
| unreduced | - | 0.195 | 0.73 | 0.167 | 0.63 |
| 1 | 2.0 | 0.168 | 0.63 | 0.155 | 0.58 |
| 2 | 3.5 | 0.119 | 0.45 | 0.113 | 0.43 |
| 3 | 2.5 | 0.107 | 0.40 | 0.103 | 0.39 |
| 4 | 3.0 | 0.100 | 0.38 | 0.098 | 0.37 |
| Sample #2 $-195^{\circ}C.$ | | | | | |
| unreduced | - | 0.154 | 0.57 | 0.133 | 0.50 |
| 1 | 2.5 | 0.117 | 0.44 | 0.112 | 0.42 |
| 2 | 2.0 | 0.100 | 0.37 | 0.098 | 0.37 |
| $-183^{\circ}C.$ | | | | | |
| unreduced | - | 0.152 | 0.59 | 0.126 | 0.49 |
| 1 | 2.5 | 0.122 | 0.47 | 0.107 | 0.42 |
| 2 | 2.0 | 0.104 | 0.40 | 0.095 | 0.37 |

as 36%, strongly suggested that only small changes in these "specific" forces occurred as a result of sintering at the reduction temperature.

Free Energy Change of Adsorption - Graham (4) developed a simple distribution function which he claimed provided the basis for a clean cut classification of physical adsorption in terms of the surface properties of the adsorbent as well as adsorbate interaction. The equilibrium constant for the transfer of one mole of adsorbate from the standard state as a liquid to the adsorbed phase can be written:

$$K = \frac{\theta}{(1-\theta)X} \tag{1}$$

where $\theta$ is the fraction of surface covered and X is the relative pressure of the gas in equilibrium with solid. The free energy change is simply given by the relationship

$$-\Delta F^O = RT \ln K \tag{2}$$

and constitutes a measure of the strength of the adsorption bond. In the ideal case involving localized, non-interacting adsorption on a uniform surface, K is a constant. Therefore, deviations of this constant from ideality can furnish information concerning the factors responsible for non-ideality such as lateral interactions between adsorbed molecules and the heterogeneous nature of the surface.

The equilibrium functions for the adsorption of argon on the second sample of the unreduced nickel and for this same sample after each of two successive reductions are shown plotted

in Figure 3 as a function of θ. The shape of the equilibrium function curve for argon adsorbed on the unreduced sample indicated adsorption on a heterogeneous surface. Initial adsorption took place on sites of high energy. Furthermore, these site energies decreased markedly with increasing θ. The equilibrium function was found to be nearly constant between θ = 0.5 to θ = 0.8, the criterion for adsorption on a uniform surface. However, a balance between cooperative adsorption and surface heterogeneity, itself, was probably responsible for the constancy of K in this region.

For the two reduced samples, the values of K were about 25 units apart at θ = 0.1 and became nearly equal as θ increased. This initial difference was evidence for the presence of surface heterogeneities at low coverages which tend to disappear as a result of sintering. Generally, it appeared from the much lower K values that the reduced samples were less heterogeneous than the unreduced nickel. Consequently, interactions between adsorbed molecules and a subsequent increase in K began at very low coverages, ca. θ = 0.2.

Isosteric Heats of Adsorption - Isosteric heat values obtained from adsorption measurements on the second nickel sample are plotted in Figure 4 as a function of the volume adsorbed. The sharp decrease in the heat values at small volumes adsorbed for the unreduced sample was of particular interest. A sharp initial decline in the heat values was found also for the reduced samples but over a smaller range of adsorption. Also, $H_0$, the

FIGURE 3

○　UNREDUCED
●　REDUCTION I
×　REDUCTION II

EQUILIBRIUM CONSTANTS K

SURFACE COVERAGE θ

FIGURE 4

○   UNREDUCED

●   REDUCTION  I

✕   "       II
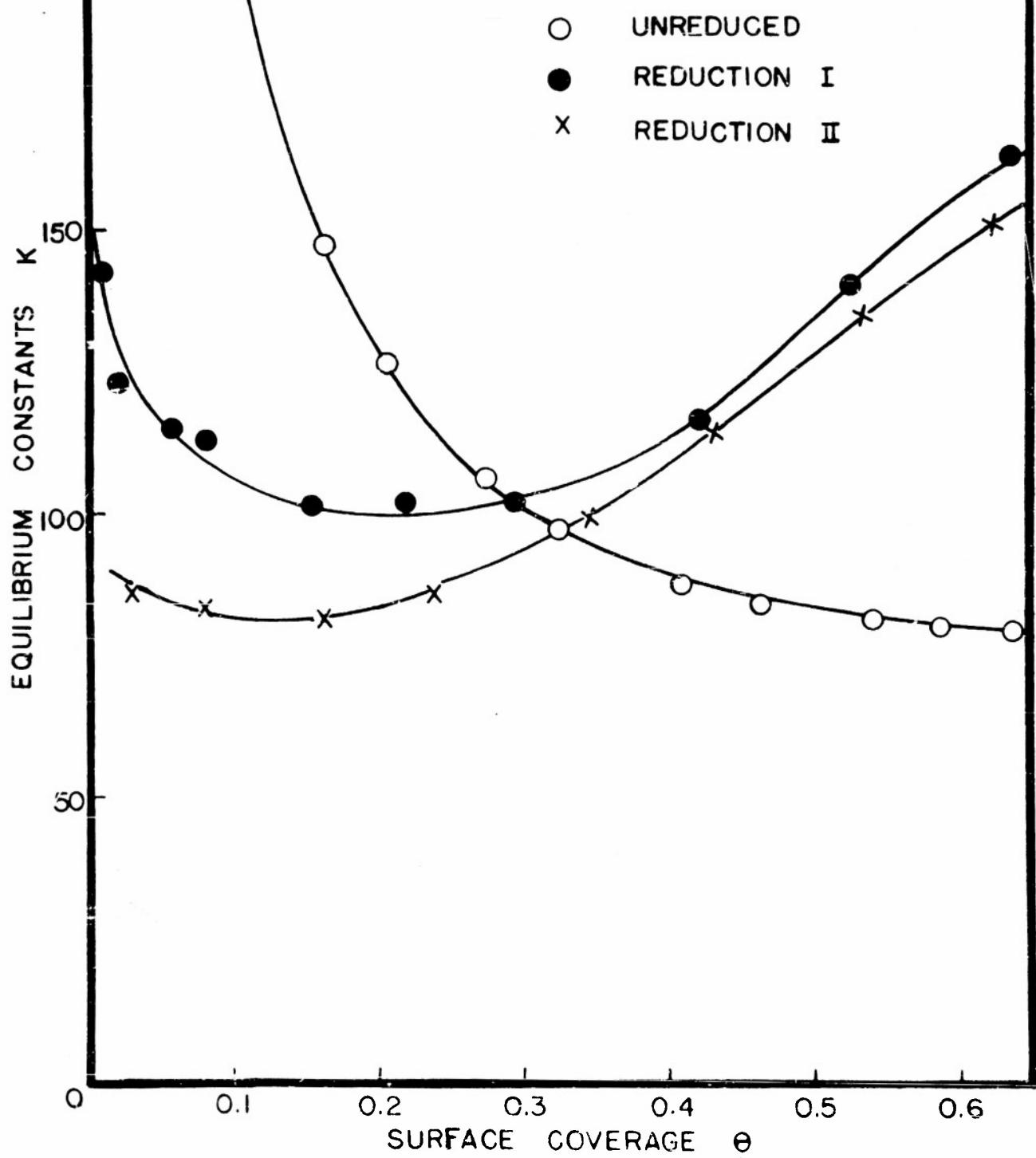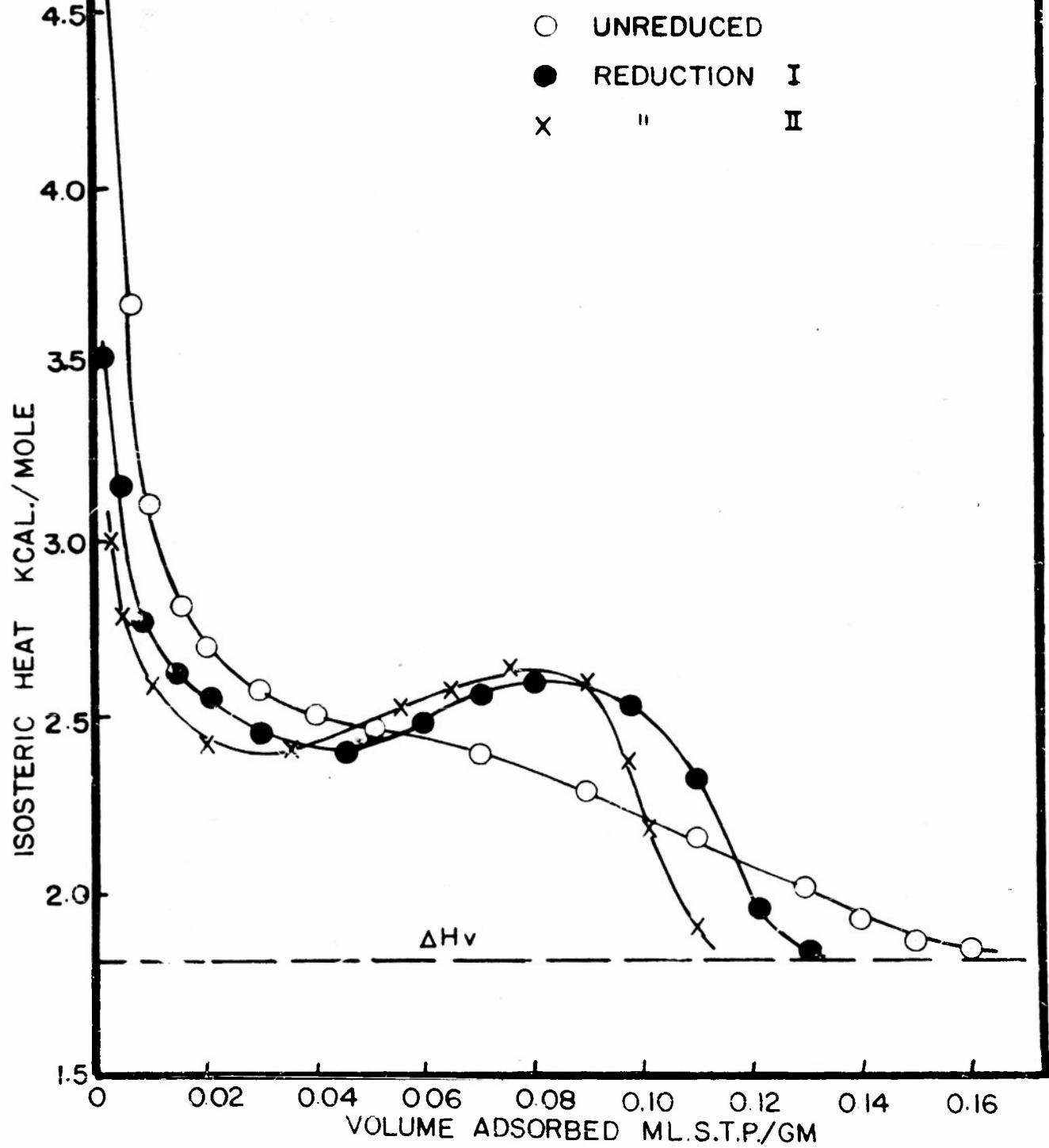
heat of adsorption at zero coverage was approximately 1.6 kcals.
greater for the unreduced sample than for this same sample after
one reduction. The rise in the heat curve and subsequent
maximum near monolayer coverage was attributable to cooperative
adsorption on the reduced surfaces. Almost exact coincidence
of the heat curves for argon adsorbed on the reduced samples
resulted if these values were plotted as a function of surface
coverage $\theta$ indicative of adsorption on the same type of surface.
However, at low values of $\theta$ the heats of adsorption were less
after the second reduction. The equilibrium function and iso-
steric heat data indicated that both the unreduced and reduced
nickel samples were heterogeneous and that these surface hetero-
geneities strongly influenced adsorption in the region of small
$\theta$ for the reduced samples and to higher values of coverage for
the unreduced nickel. Furthermore, the surface heterogeneities
on the reduced samples tended to smooth out as a result of
sintering at the high temperature employed in the reduction.

Absolute Entropy of the Adsorbed Phase - Hill (2) showed
that on a model of localized adsorption on a heterogeneous surface
without adsorbate interactions the configurational entropy at
temperature T is given by the equation:

$$S_c = k \ln \frac{B_i!}{N_i!(B_i-N_i)!} \qquad (3)$$

where $B_i$ represents the sites of energy $i$ and $N_i$ the number of
molecules adsorbed on the $B_i$ sites. The maximum possible con-
figurational entropy $S_m$ (T infinite) is expressed by the relation-

ship:

$$S_m = k \ln \frac{B!}{N!(B-N)!} \qquad (4)$$

and is independent of the distribution of site energies on
the surface. $S_m$ also gives the configurational entropy on a
uniform surface. Drain and Morrison (3) carried out the
arduous  alculations necessary to obtain the configurational
entropy from equation 3 as well as the non-configurational
entropy for the adsorption of argon on rutile at $85^{\circ}$K. A know-
ledge of the site energy distribution for argon adsorbed on
this solid at $0^{\circ}$K was essential to their calculations and this
in turn was obtained from calorimetric measurements of the heat
capacities of adsorbed argon films down to very low temperatures.
These heat capacity measurements probably represent the only
method presently available to obtain a distribution function at
$0^{\circ}$K where the surface sites fill strictly in order of their
energies.

Since it was impossible to obtain a proper distribution
function for the argon-nickel systems studied here, the rigorous
calculations of the type outlined by Hill could not be carried
out. However, on the basis of the model outlined previously,
the integral molar configurational entropy is represented reason-
ably well by the equation

$$S_c = \frac{\pi^2}{3} \cdot R \cdot \frac{d \ln V}{d \ln p} \qquad (5)$$

This expression 5 is accurate for a site energy distribution
wide compared to RT and should not be in error by more than 20%

even for a homogeneous surface below monolayer coverage (3).

In Figure 5 the experimental molar entropies, $S_S$, for argon adsorbed on unreduced nickel and this sample after one reduction are plotted as a function of surface coverage, $\theta$. The general shapes of the two curves were similar; i.e., both showed an increase in entropy with increasing adsorption in the range of low $\theta$ values and then remained little changed as coverage increased. The absence of high entropy values in the region of small $\theta$ was surprising for this adsorbate at this temperature and suggested that adsorption here took place on very heterogeneous portions of the surfaces with small contributions to the total entropy due to configurational effects and particularly so for the unreduced sample.

For localized adsorption on a heterogeneous surface, configurational entropies calculated from equation 5 should be valid for the argon-nickel systems up to the point where interactive adsorption began. Calculated configurational entropy values for both nickel surfaces are compared in Figure 5. These values were one to two entropy units lower for the unreduced surface and supported the contention based on previous data that this unreduced surface was the most heterogeneous of the two types studied. Furthermore, the configurational entropies for both surfaces tended toward zero as $\theta$ 0, a fact already deduced from the shapes of the integral entropy curves at low $\theta$.

The calculated, $S_C$, curves increased with increasing coverage and eventually exceeded the maximum possible configu-

FIGURE 5
UNREDUCED   REDUCED
O      ☻
O      ●
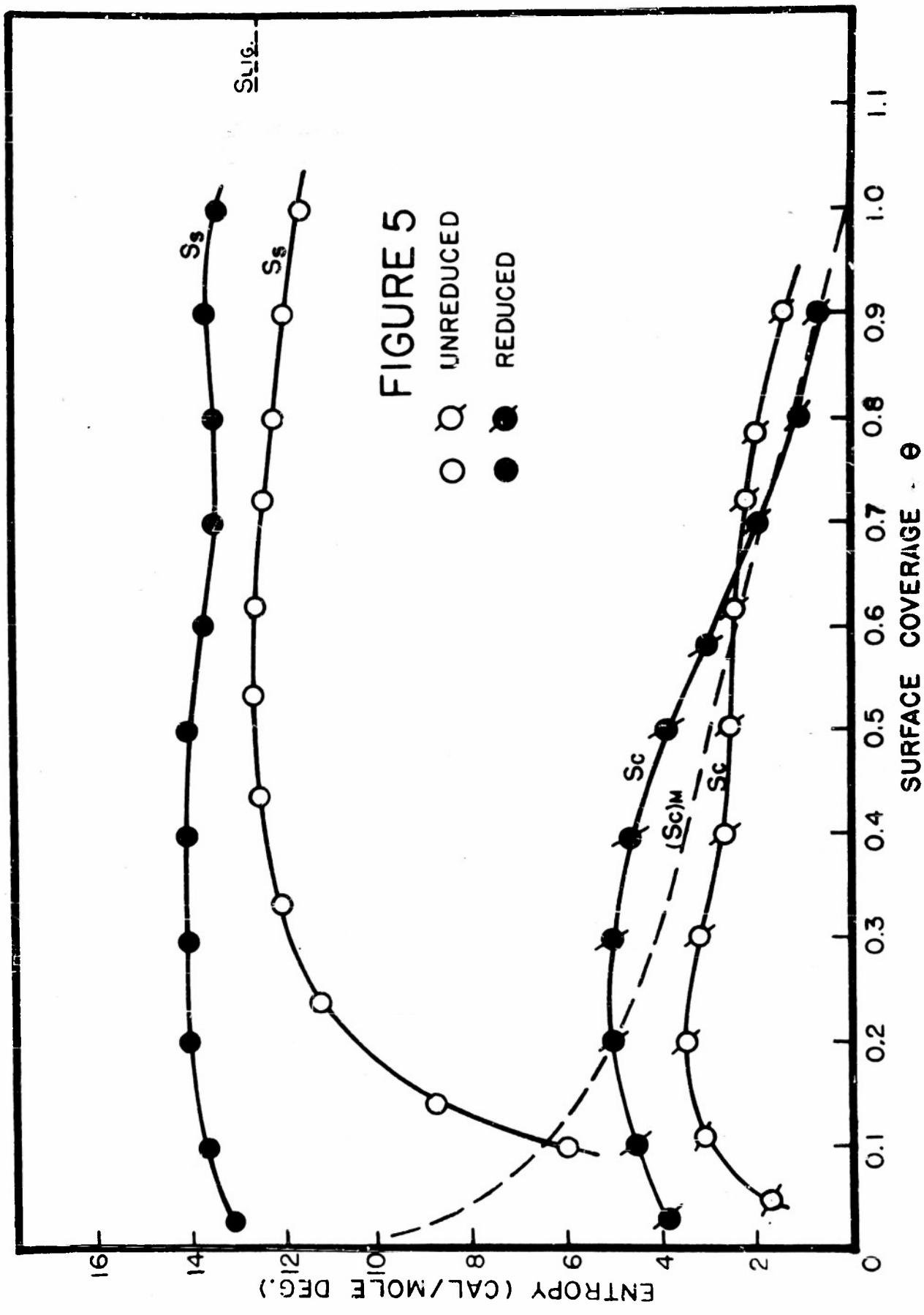
rational entropy, $S_m$. For the reduced sample, this took place at $\theta \sim 0.2$ and undoubtedly was evidence for the onset of adsorbate interactions at unusually low coverages. The equations developed by Hill (2) to treat adsorption on a heterogeneous surface with nearest neighbor interaction were too complex to treat mathematically even if a proper distribution function were available. Thus it was likely that a model of localized adsorption on a heterogeneous surface without adsorbate interaction was not valid beyond $\theta = 0.2$ and $\theta = 0.5$ for the reduced and unreduced surfaces respectively.

In the presence of interactions a division into a non-configurational and configurational entropy becomes arbitrary. Thus, it becomes difficult to interpret the essentially constant entropy values at higher coverages. These values are very near the entropy of liquid argon for both samples.

## Acknowledgment

A VOLUMETRIC CALORIMETER FOR
HEATS OF IMMERSION OF SOLIDS
INTO LIQUID NITROGEN


## INTRODUCTION

Immersional calorimetry for the study of systems at
or near room temperatures has been well developed (1,2,3),

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(1)   G.E. Boyd and W.D. Harkins, J. Am. Chem. Soc., 64, 1190
      (1942)

(2)   E. Hutchinson, Trans. Faraday Soc., 43, 443 (1947)

(3)   A.C. Zettlemoyer, G.J. Young, J.J. Chessick, and F.H.
      Healey, J. Phys. Chem., 57, 649 (1953)

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and has lead to valuable data concerning the interaction

between surface and adsorbate supplemental to that obtained

from gas adsorption studies. To obtain such information

from the immersion of a solid in a liquid whose normal

temperature is far removed from room temperature special

procedures are required to detect the minute temperature

changes resulting from the wetting of a solid by the liquid.

A simple and accurate method has been developed for

the measurement of the heats of immersion of solids in liquid

nitrogen at its boiling point at $-195°$. This technique, the

measuring of the volume of liquid vaporized, requires none of

the elaborate and expensive equipment usually used in immers-

ional calorimetry and, in addition, can be applied to the

immersion of solids in other liquids at their boiling points.

## EXPERIMENTAL

Low Temperature Immersional Calorimeter: The low temperature calorimeter is shown in Figure 1. Heat effects are measured by the amount of liquid nitrogen which is vaporized and collected as a gas when a clean sample is broken under the liquid. The calorimeter consists of two sections of a large glass tube joined by means of a 45/50 standard taper joint. A hollow tube, A, with a shield, B, to prevent spattering of liquid nitrogen is sealed to the upper calorimeter section. The breaker rod, C, passes through this tube and rests on top of the sample tube, D. A tight fitting piece of rubber tubing is used to form an air tight seal between this tube and the breaker rod; the tubing allows sufficient movement of the rod to break the sample tube. The exit tube, E, is connected to a gas burette by means of rubber tubing. The calorimeter is immersed in a large Dewar flask containing liquid nitrogen. Liquid nitrogen is introduced into the calorimeter, itself, through tube, E.

Sample Tube Breaking: The sample tubes are specially constructed so that the bottoms have very thin walls. The tubes rest on a formed rubber support with the breaker rod immediately above the thin wall portion. A light tap of the breaker rod is sufficient to pierce the sample tube. Blank runs indicate that the heat effect resulting from breaking in this manner is so small that it contributes only from 5 to 15 ml. to the total amount of gas evolved. A cor-

RUBBER GASKET

TO GAS MEASURING BURETTE

E

C

A

STANDARD TAPER JOINT

B

LIQUID NITROGEN

D

FIGURE 9

LIQUID NITROGEN IMMERSION CALORIMETER
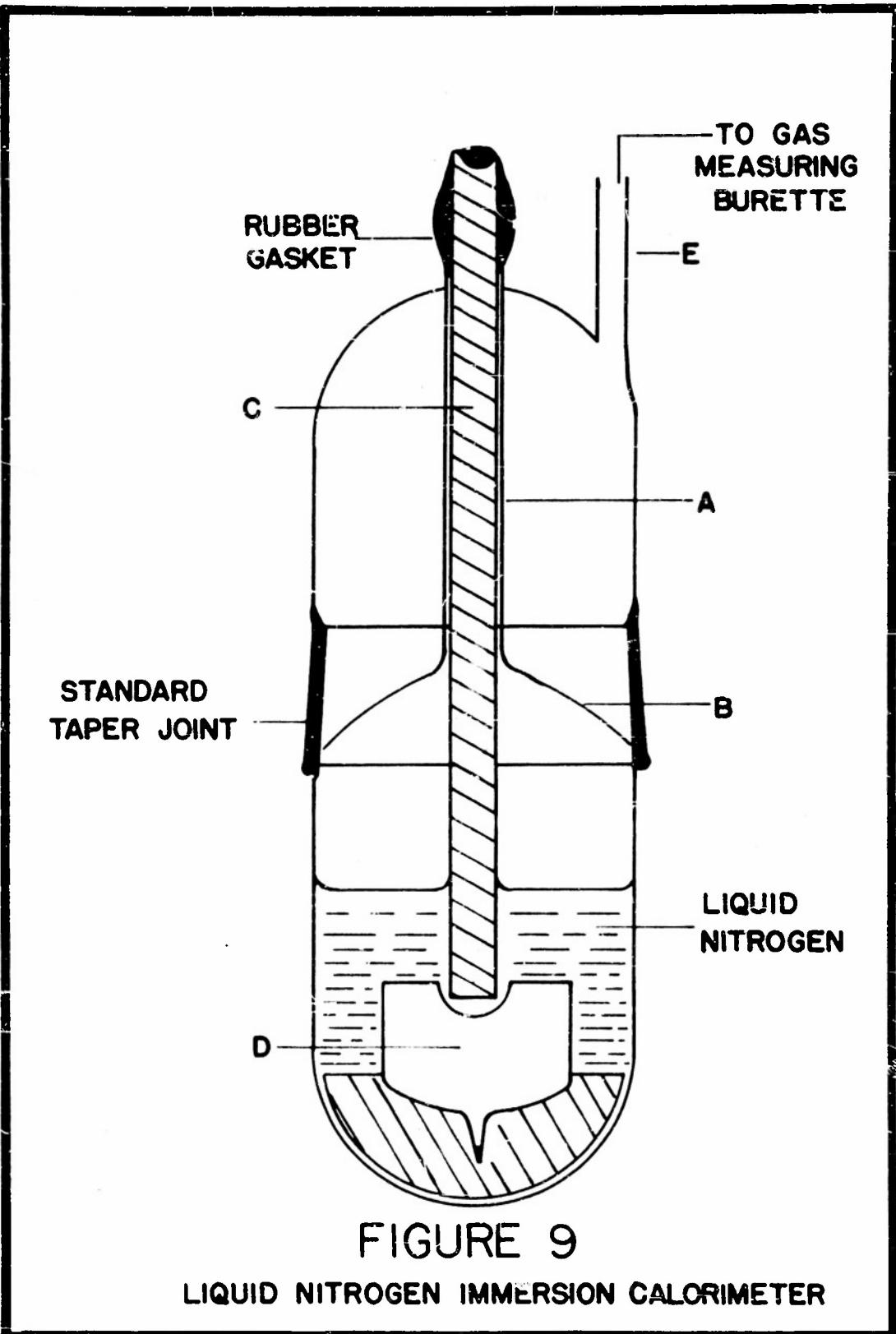
rection of 10 ml. was applied to all measurements.

Rating Periods: Once temperature equilibrium between the calorimeter and bath is reached the amount of nitrogen gas evolved each minute is determined by displacement of water from a gas burette. The amount of gas evolved was found to be constant for periods of 0.5 to 1.0 hours, and is a function of the purity of liquid nitrogen used and the barometric pressure; the most pronounced influence, however, is that produced by the latter. The rates varied from 20 to 50 ml. of gas evolved per minute using commercial liquid nitrogen with measured vapor pressures between 79 and 82 cm. Hg. No runs were made using a particular liquid nitrogen supply if the rating period exceeded 50 ml. per minute.

Procedure: For the results described below, samples weighing 4 to 10 grams were evacuated under the conditions listed in Table I, then were sealed off under vacuum and transferred to the calorimeter. Before joining the two sections of the calorimeter, Apiezon "M" grease was applied to the standard taper joint. The entire calorimeter was placed in a large Dewar flask and liquid nitrogen was added to the flask until the liquid level was about one-inch above the top of the calorimeter. After a few minutes 250 ml. of liquid nitrogen was added to the calorimeter, itself, through the exit tube. Rubber tubing leading to the gas burette was then attached to the exit tube and the displacement of water

by the nitrogen gas evolved was noted. The maximum time for temperature equilibrium between the calorimeter and bath to be reached was three hours. A time-gas volume curve was followed until a steady rate of gas evolved was obtained over a ten minute period. The sample was broken under the liquid and the time noted. Time-volume readings were continued for 10-15 minutes after breaking. The heat of immersion was always evolved within less than one minute after breaking. The smallest volume of gas evolved was about 100 ml. (STP); the average volume was about 200 ml.

The gas evolved as a result of the wetting process was corrected for the height of the column of water in the gas burette, as well as for the presence of water vapor, then converted into ml. evolved at STP. The heat of immersion in ergs/cm$^2$. was calculated from the formula:

$$h'_{(SL)} = - \frac{\Delta V(ml. STP)}{22,400} \left| \frac{1333}{wt.} \right| \frac{4.187 \times 10^7}{area} \, cm^2./g.$$

where 1333 cal./mole is the heat of vaporization of liquid nitrogen.

Adsorption Measurements: Isotherm data at 77.8 and 72.3°K for the adsorption of nitrogen on magnesia "2642" were selected from the results of a study previously conducted in this laboratory; a detailed discussion of these earlier experimental techniques has been fully described (4).

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(4)  A. C. Zettlemoyer and W. C. Walker, Ind. and Eng. Chem., 39, 69 (1947).

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Experimental Results and Reproducibility. Values of
the heats of immersion for a variety of solids from liquid
nitrogen are tabulated in Table I. The average deviation
represents a measure of the reproducibility of the results.
The maximum deviation amounts to about 5% which is good
agreement because a combination of factors such as weighing,
pretreatment, activation and evacuation of the samples as
well as direct calorimetric measurements affect these values.

TABLE I

Heat of Immersion of Solids in Liquid Nitrogen at $-195^{\circ}$

| Sample | Specific Area $m^2./g.$ | Heat of Immersion $ergs/cm^2.$ | Number of Determinations | Activation Time hrs. | Temp. $^{\circ}C.$ |
|--------|--------|--------|--------|--------|--------|
| Graphon [a] | 83.0 | $-104\pm1$ | 3 | 24 | 25 |
| Silene (EF) [b] | 51.6 | $-102\pm1$ | 3 | 24 | 25 |
| Alumina (F10) [c] | 119.2 | $-104\pm5$ | 4 | 2 | 400 |
| Magnesia "2642" [d] | 112.7 | $-105\pm4$ | 4 | 1 | 250 |

(a)  Lot L-2739, Godfrey L. Cabot Co., Boston, Mass; a graphitized
     carbon black: the maximum amount of surface oxide has been
     estimated to occupy no more than 1/1500 of the total area.
     "Thermodynamics of the Adsorption of Water on Graphon", G. J.
     Young, J. J. Chessick, F. H. Healey and A. C. Zettlemoyer, to
     be published J. Phy. Chem. about May 1954.
(b)  Ppt. Calcium Silicate, Pittsburg Plate Glass Co., Pittsburg, Pa.
(c)  Lot 202, 8-14 mesh, Aluminum Co. of America, Pittsburg, Pa.
(d)  Furnished by Westvaco Chemicals Division, Food Machinery
     Corporation.

An important observation is the fact that the values of the heats of emersion are practically the same for these four different solids. Since the surfaces of these solids are considerably different, especially the hydrophobic Graphon, this finding suggests that the volume of gas evolved when one gram of a clean solid is immersed in liquid nitrogen may be taken as a measure of the specific area.

## DISCUSSION

When a nonporous solid is immersed in a liquid, the solid surface with its energy disappears and is replaced by a solid-liquid interface. The heat of emersion (5) for the

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(5) Because of the convention established by W. D. Harkins, the heat of emersion will be discussed in the theoretical section of this paper. Furthermore, the definition of the spreading pressure $\varphi = \gamma_S - \gamma_{S\varphi}$ has been conventionally established for the desorption process.

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process is given by the relationship:

$$h_{SL} = \left[ \gamma_S - \gamma_{SL} - T \left( \frac{\partial \gamma_S}{\partial T} - \frac{\partial \gamma_{SL}}{\partial T} \right) \right]_{P, \Sigma} \quad (1)$$

where $\gamma_S$ and $\gamma_{SL}$ are the free surface energies of the clean solid and the solid-liquid interface at temperature T, and $\Sigma$ is the surface area of the solid. The value of $h_{SL}$ for the emersion of MgO from liquid nitrogen at $-195^\circ$ was obtained experimentally and compared to values calculated by two methods using adsorption data. It was pertinent to inquire, also, into the relative importance of the contributions to the heat of

emersion for this process by both the free energy and entropy terms.

Calculated Heat of Emersion from Isosteric Heats of Adsorption: The difference in the internal energy, $E_L$, of a liquid adsorbate in equilibrium with vapor at T, and the energy, $E_a$, of the adsorbate molecules is given by the relationship (6)

(6)  G. Jura and T.L. Hill, J. Am. Chem. Soc., 74, 1498 (1952).

$$E_L - E_a = (h_{SL} - h_{S_fL})/N_a \qquad (2)$$

where $h_{SL}$ and $h_{S_fL}$ are the heats of emersion of a clean solid and a solid with $N_a$ adsorbed molecules. The term is related to the isosteric heat, $q_{ST}$, by an equation readily obtained from Equation 91 of Hill (6)

(6)  T.L. Hill, J. Chem. Phys., 17, 520 (1949)

$$h_{SL} - h_{S_fL} = \int_0^{N_a} q_{st} \, dN_a - N_a \Delta H_v \qquad (3)$$

where $\Delta H_v$ is the molar heat of vaporization of nitrogen. The term $h_{SL} - h_{S_fL}$ can thus be obtained by graphical integration of a $q_{ST}$ vs. $N_a$ plot.

The heat of immersion of a solid, which has been exposed to the saturated vapor of the liquid until the adsorbed film attains equilibrium with respect to the vapor, is given by the equation (7):

(7)  W.S. Harkins, "The Physical Chemistry of Surface Films",
New York, Reinhold Publishing Co., 1952, pg. 274.

$$ h'_{SL} = -\left[ \left( \gamma_L - T \frac{\partial \gamma_L}{\partial T} \right) \cos \theta + T \gamma_L \sin \theta \frac{\partial \theta}{\partial T} \right] \quad (4) $$

where $\gamma_L$ is the free surface energy of the liquid and $\theta$ is
the contact angle of the liquid on the surface. If $\theta = 0$, then
the heat of emersion is

$$ h_{S_E L} = \left[ \gamma_L - T \left( \frac{\partial \gamma_L}{\partial T} \right) \right] = h_L \quad (5) $$

Equation (5) represents the heat content of the surface of
the liquid used. The value of this quantity for liquid
nitrogen (25.2 ergs/cm$^2$, at 74.9° K) was obtained from the sur-
face tension and temperature variation of the surface tension
of the liquid. The heat of emersion, $h_{SL}$, of clean MgO was
calculated to be 110 ergs/cm$^2$. from a knowledge of $h_L$ and the
differences in the heats of emersion at saturation obtained
from equation (3). This value compares with the value of 105
ergs/cm$^2$. found experimentally.

The calculated values for the heat of emersion of MgO
are shown plotted in Figure 2 as a function of the volume of
nitrogen adsorbed. The heat values approach the value for the
heat content of a liquid nitrogen surface only at high surface
coverage, ca. 10 molecular layers (8).

FIGURE 2
HEAT OF IMMERSION
MAGNESIA INTO
LIQUID NITROGEN
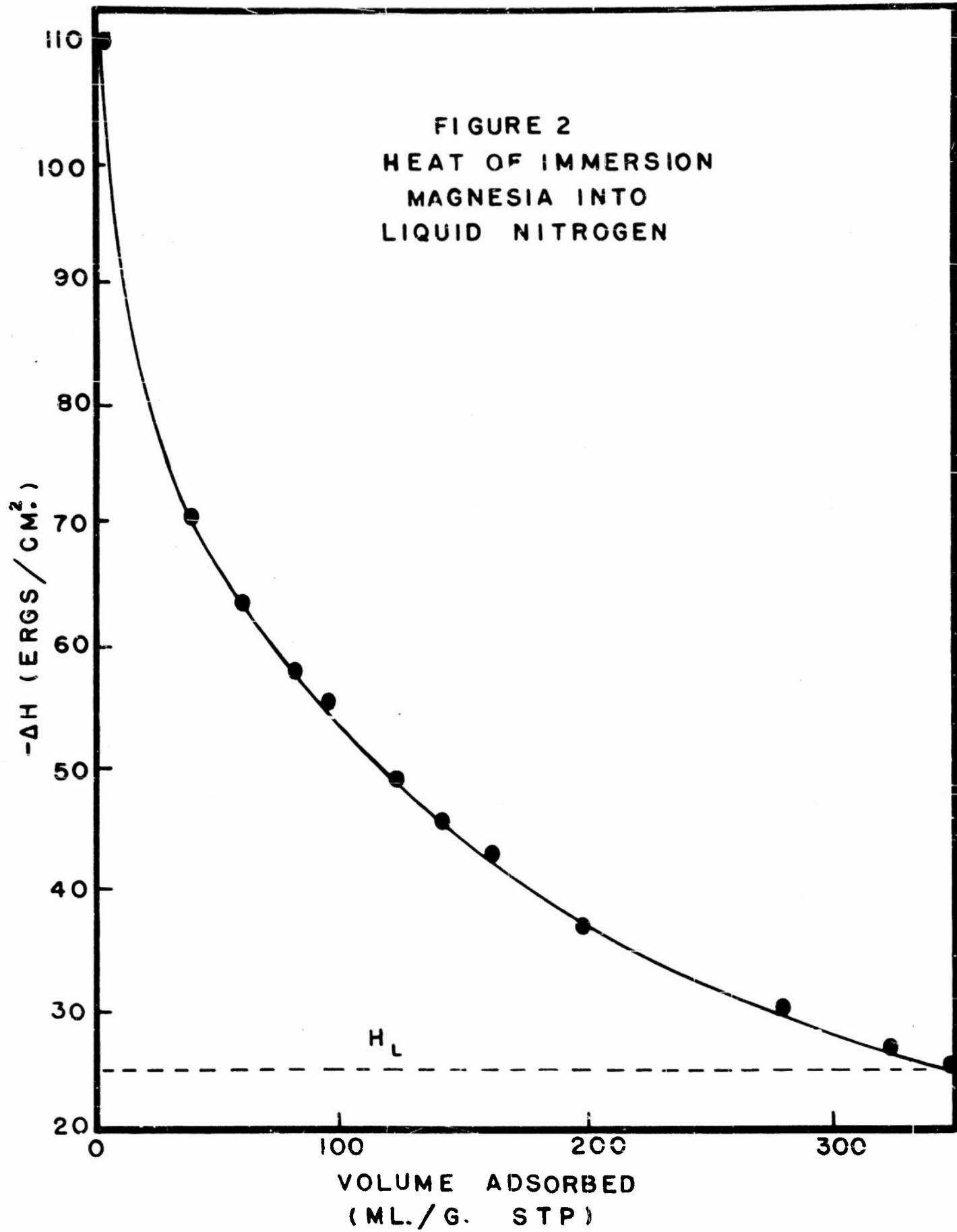
(8)  In contrast, heat values for the emersion of asbestos
     from water approach the surface enthalpy of liquid
     water very nearly after the completion of a mono-
     molecular layer (3).

Calculated Heat of Emersion from Absolute Entropy Values:
The equilibrium heats of adsorption, $H_G - H_a$ and the corresponding
integral entropy values, $S_G - S_a$ where the subscript, G, refers
to gaseous nitrogen in equilibrium with the adsorbed film, a,
were calculated for the adsorption of nitrogen on MgO (9.

(9)  T.L. Hill, J. of Chem. Phys., 17, 520 (1949)

The equilibrium heats were obtained from the Clausius-Clapeyron
equation at constant spreading pressure, $\varphi$.  Thus it was necessary
to determine $\varphi$ as a function of the equilibrium pressures at two
temperatures from adsorption data by graphical integration of the
Gibbs equation:

$$\varphi = \gamma_s - \gamma_{sf} = kT \int_0^p \Gamma \, d \ln p \qquad (6)$$

where $\Gamma$ is the surface concentration.  The equilibrium and
isosteric heats of adsorption are plotted in Figure 3 as a
function of the volume adsorbed.

     When the contact angle of a liquid on a solid is zero,
and, further, if the film formed on a solid in equilibrium with
the saturated vapor of the liquid is duplex then

$$\gamma_{S_a} = \gamma_{SL} + \gamma_L \qquad (7)$$

FIGURE 3
ISOSTERIC & EQUILIBRIUM
HEATS OF ADSORPTION
NITROGEN ON MAGNESIA
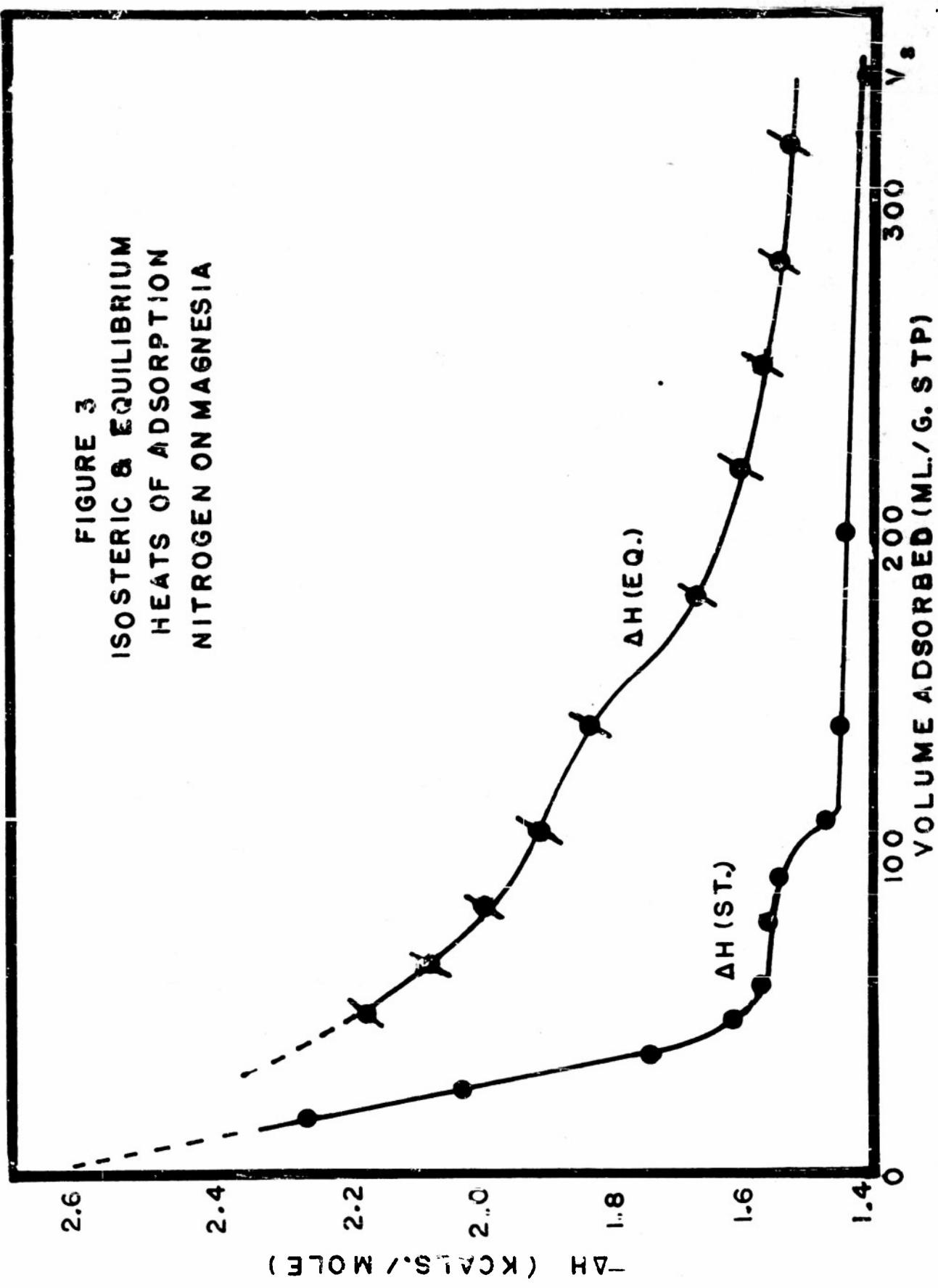
and equation (1) can be written in the form

$$h_{SL} = \left[ \varphi_e + \gamma_L - T\left(\frac{\partial \varphi_e}{\partial T}\right) - T\left(\frac{\partial \gamma_e}{\partial T}\right) \right] \qquad (8)$$

The temperature coefficient, $\partial \varphi_e / \partial T$, of the difference in the free surface energy of a clean solid and a film covered solid is related to the difference in the integral entropy term

$$\partial \varphi_e / \partial T = -N_a k \ln X + N_a (S_a - S_L) \qquad (9)$$

At saturation the relative pressure, X, of the gas in equilibrium with the adsorbed film is equal to unity, thus

$$\partial \varphi_e / \partial T = N_a (S_a - S_L) \qquad (10)$$

The term $(S_a - S_L)$ was obtained from the equilibrium heat of adsorption at saturation and a knowledge of the entropy of vaporization of liquid nitrogen at $74.9°$K.

Table II contains values for measured and calculated quantities used to obtain the heat of emersion of magnesia from liquid nitrogen. A value of 117 ergs/cm$^2$. was calculated from equation 8. The $\partial \varphi_e / \partial T$ term was obtained from entropy data (eqn. 10). This value of 117 agrees fairly well with the value of 110 ergs/cm$^2$. obtained from isosteric heat data (eqn. 3) as well as with the experimental value of 105 ergs/cm$^2$. It is also evident from Table II that the $T\Delta S$ term contributes most to the heat term, that is about three times more than the free energy contribution.

## TABLE II

### Free Energy and Entropy Values

| Terms | Values ergs/cm$^2$ deg. | | |
|---|---|---|---|
| $\partial(\gamma_s - \gamma_{se})/\partial T$ | $-0.92$[a] | | |
| $\partial(\gamma_s - \gamma_{sL})/\partial T$ | $-1.22$ | | |
| | ergs/cm$^2$ | | |
| $\gamma_L$ | $9.39$ | | |
| $\partial \gamma_L/\partial T$ | $-0.22$ | | |
| $\gamma_e$ | $22.3$ | | |
| $h_{sL} - h_{seL}$ | | $85.0$ | |
| $h_{seL}$ | | $25.2$ | |
| $\Delta F = \gamma_s - \gamma_{sL}$ | $31.7$ | | |
| $T\Delta S = T[\partial(\gamma_s - \gamma_{sL})/\partial T]$ | $85.5$ | | |
| $\ell_{sL}$ | $117.0$[b] | $110.0$[c] | $105 \pm 4$ exp. |

(a) from eqn. 10.

(b) from eqn. 8, based on entropy values.

(c) from eqn. 3, based on isosteric heat values.

THE DETECTION OF HYDROPHILIC HETEROGENEITIES
ON A CARBON SURFACE

## INTRODUCTION

The purpose of this investigation was to study
the effect of surface heterogeneity on the adsorption of
water on a hydrophobic surface. The system Graphon-water
was chosen because Graphon possesses a well-defined hydrophobic
and almost homogeneous surface with a very small fraction of
hydrophilic heterogeneities (1,2) which are responsible for

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(1)  Pierce and R.N. Smith, J. Phys. and Colloid Chem. 54,
     784 (1950).

(2)  G.J. Young, J.J. Chessick, F.H. Healey, and A.C. Zettlemoyer,
     J. Phys. Chem. 58, 313 (1954).

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the adsorption of water at low pressures. It appeared possible
to increase the fraction of hydrophilic sites by controlled
oxidation of the Graphon and to observe the changes produced in
the water adsorption isotherm and the heat of immersion in water.
It was of interest to determine the relation between the heat of
immersion and the fraction of surface which was hydrophilic.

The application of the BET equation to the adsorption
of water on Graphon has been shown to give values consistent with
the thermodynamic criteria of a complete monolayer (2). Unpub-
lished work in this laboratory with known mixtures of a hydrophilic
surface, rutile, and a hydrophobic surface, Graphon, has demon-

strated that the ratio of the apparent surface area determined by water adsorption to the total area determined by nitrogen adsorption is a direct measure of the fraction of hydrophilic surface present in the mixture. Accordingly this ratio has been used in the present work to characterize the hydrophilic heterogeneity of the Graphon surface before and after oxidation.

## EXPERIMENTAL

Materials and Apparatus - The Graphon sample was from the same lot, No. 2808, as used previously (2) and was supplied by Godfrey L. Cabot, Inc. The area determined by nitrogen adsorption was 98 m.$^2$/g., and the freshly prepared sample was reported to contain 0.25% ash and 0.2% volatile matter. The samples were not treated with hydrogen since it was desired to preserve any heterogeneous surface sites.

High purity nitrogen, helium, oxygen and water were used and further purified by procedures previously described (3).

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(3) A.C. Zettlemoyer and J.J. Chessick, J. Phys. Chem., 58, 242 (1954).

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Nitrogen adsorption and static oxidation studies were made with a BET type adsorption apparatus; water vapor adsorption measurements and procedures using a modified Orr apparatus have been described (2).

Dynamic Oxidation - Tank oxygen at 1 atmosphere without further purification was passed slowly through the samples

at 530° for various time periods (listed in Table I). The
Graphon sample was then cooled to room temperature and de-
gassed at $10^{-5}$ mm. Hg. A portion of the sample was used
for adsorption measurements and the remainder subjected to
further oxidation under the same conditions.

Static Oxidation - The samples were degassed at
room temperature for 12 hours before oxidation. Moist
oxygen, made by mixing known volumes of water vapor and dry
oxygen to obtain a relative humidity of ca. 0.5, was admitted
to the sample at room temperature and the equilibrium pressure
recorded. The sample was then heated to 530° within a time
interval of ten minutes. The total pressure at this tempera-
ture was approximately one atmosphere. The temperature was
controlled to ± 5° throughout the oxidation and any changes
in pressure were noted. After two hours the sample was cooled
to room temperature and the final equilibrium pressure was
recorded.

Adsorption Measurements - About 0.5 grams of Graphon
was used for nitrogen surface area determinations at -195°.
The surface areas were calculated by the BET method using a close-
packed adsorbate area of 16.2 $\overset{o}{A}^2$. Water vapor adsorption measure-
ments were made at 25° with 5 to 0.5 gram samples depending on
the extent of oxidation of the surface. An experimental deviation
of 0.005 ml. adsorbed was observed at the lower pressures.

With one sample the weight change caused by successive
oxidations was followed. After each oxidation water vapor was

admitted to a relative pressure of 0.3, at which pressure, as determined by the volumetric measurements, the BET $V_m$ value was reached. The amount of water adsorbed was then measured gravimetrically with a correction made for the vapor in the dead space. The results agreed with the volumetric measurements within experimental error.

Heat of Immersion Measurements - The calorimeter and procedure have been described earlier (4). Heats of

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(4) A.C. Zettlemoyer, G.J. Young, J.J. Chessick and F.H. Healey, J. Phys. Chem., 57, 649 (1953).

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immersion in water were measured for Graphon after the various types of treatment given below.

Treatment of Samples - Sample A was oxidized by the dynamic process. Sample B received the static oxidation treatment with nitrogen and water vapor adsorption determined volumetrically. A second sample treated and measured in the same way checked the results obtained with Sample B. Sample C was activated at 900° for two hours with continuous pumping to study the thermal decomposition of the heterogeneous surface sites present on the original sample. Sample D received the same oxidation treatment as sample B but weight losses on oxidation and water adsorption measurements were made gravimetrically.

When this work was initiated it was hoped that the number of surface oxide sites formed could be directly measured from the oxidation data. However the complexity of the oxidation

process (5) and particularly when water was present (6) pre-

(5)  E.A. Gulbransen, Ind. Eng. Chem., 44, 1045 (1952).

(6)  R. Smith, C. Pierce, and C.D. Joel, J. Phys. Chem. 58, 298 (1954).

vented any direct determination of the amount and nature of the surface oxide formed. A further complication was introduced when it was found the $O_2$, CO, and particularly $CO_2$ all showed some physical adsorption on Graphon at room temperature. The isotherms were linear and at 20 mm. Hg. pressure the respective volumes adsorbed were 0.0055, 0.0090 and 0.029 ml./g.

## RESULTS AND DISCUSSION

The apparent surface areas determined by application of the BET equation to the adsorption isotherms of water vapor and nitrogen on Sample A after various times of dynamic oxidation are given in Table I. The apparent area available to water vapor adsorption increased, as was expected, with increasing time of oxidation. The nitrogen or "true" surface area also increased markedly, the final area of 181 m.$^2$/g. being roughly double the original value. The ratio of the apparent water area to the nitrogen area can be considered to be a measure of the surface heterogeneity, i.e., the fraction of hydrophilic sites present on the surface. The ratio may also be considered to be a measure of hydrophobicity; the smaller the ratio, the more hydrophobic the surface. The original sample had a surface with only about

TABLE I

Dynamic Oxidation at $530^\circ$ - Sample A

| Total Time of Oxidation (hrs.) | Apparent BET Area (m.$^2$/g.) | | $\dfrac{\Sigma H_2O}{\Sigma N_2}$ x $10^2$ |
| :---: | :---: | :---: | :---: |
| | $\Sigma H_2O$ | $\Sigma N_2$ | |
| 0 | 0.26 | 93.0 | 0.27 |
| 2 | 1.06 | 110.3 | 0.96 |
| 3 | 2.05 | 114.2 | 1.80 |
| 5 | 3.52 | 135.7 | 2.24 |
| 10 | 12.45 | 152.0 | 8.20 |
| 17 | 22.52 | 180.9 | 12.44 |

1/400 of the surface hydrophilic; after 17 hours of oxidation about 1/8 of the surface had become hydrophilic. In other words about one-eighth of the surface had been oxidized by this treatment. At the same time a considerable portion of the sample was lost; the sample weight used in the last oxidation 0.42 g. and after 7 hours this weight had been reduced to 0.09 g.

The oxidations carried out in a static, moist, oxygen atmosphere were much less drastic in their effect on the sample as shown in Table II. The nitrogen surface area increased by only 5% after 12 hours of oxidation compared to an increase of over 50% after ten hours of dynamic oxidation. Further, at this point only about 1/70 of the surface had been oxidized.

The sample activated at $900^\circ$ showed only a slight increase in the nitrogen surface area and a marked decrease in

## TABLE II

### Static Oxidation - Sample B

| Total Time of Oxidation (hrs.) | Apparent BET Area (m.$^2$/g.) | | $\dfrac{\Sigma H_2O}{\Sigma N_2}$ x $10^2$ |
|---|---|---|---|
| | $\Sigma H_2O$ | $\Sigma N_2$ | |
| 0 | 0.26 | 98 | 0.27 |
| 2 | 0.50 | 101 | 0.50 |
| 4 | 0.64 | 103 | 0.62 |
| 6 | 0.85 | 102 | 0.83 |
| 8 | 0.96 | 102 | 0.94 |
| 10 | 1.16 | 103 | 1.13 |
| 12 | 1.44 | 102 | 1.41 |
| Sample C Activated, 900°, 2 hrs. | 0.15 | 100 | 0.15 |

the number of hydrophilic sites, presumably due to volatilization of carbon-oxygen surface complexes.  About 45% of the hydrophilic sites were destroyed by activation.

To demonstrate the effect of increasing the percentage of hydrophilic heterogeneity on the adsorption of water, the isotherms at 22° after the various static oxidation treatments are shown on the next page.  It is evident that the successive oxidations caused a continual increase in the volume of water adsorbed at all relative pressures.  The adsorption isotherm reported by Pierce and Smith (7) for water on Graphon which had

(7) C. Pierce and R.N. Smith, J. Phys. and Colloid Chem. 54, 795 (1950).
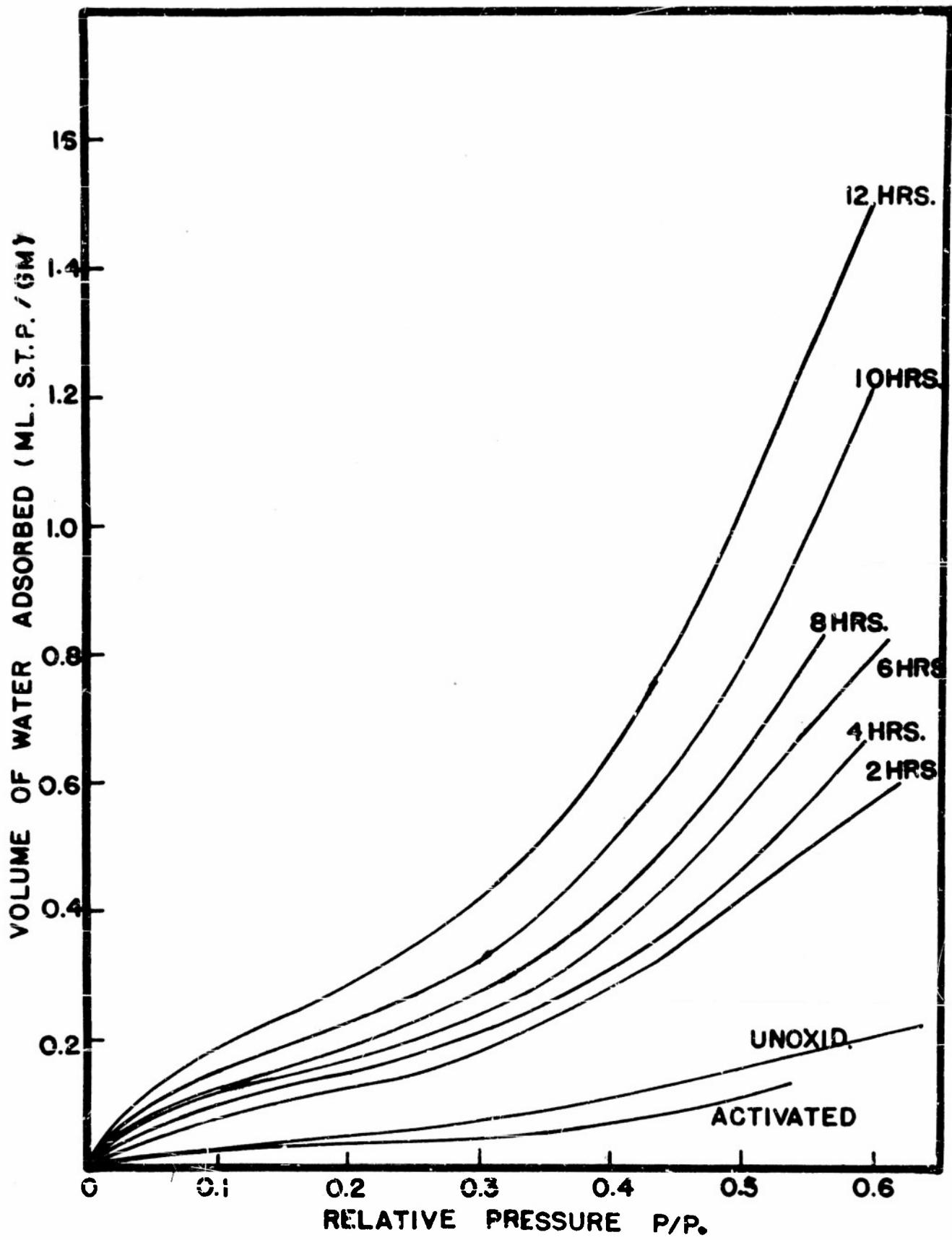
been treated with hydrogen at 1100° would lie slightly above the curve for the original (unoxidized) sample. Since their sample had a nitrogen surface area about 20% less than the present Graphon, their surface must have still contained after treatment a considerable amount of hydrophilic heterogeneities. Recently it was reported (6) that the earlier Graphon contained considerable more sulfur than more recent samples and this may be the cause of the greater water up-take.

The increase in the fraction of hydrophilic sites appeared to increase approximately linearly with time of oxidation although there was considerable scatter due in part perhaps to the uncertainty in choosing the best straight line in the BET plots used to obtain $\Sigma \, H_2O$. The rate of apparent surface oxidation, assuming one molecule of $H_2O$ adsorbed per oxide site at $V_m$, was $0.0019 \pm .0005$ surface sites per hour. With Sample D where the static oxidation was carried to 20 hours and the water pick-up determined gravimetrically the curve was shown to be actually parabolic, and that furthermore, the sample showed a considerable loss in weight. The rate of increase in the fraction of hydrophilic sites cannot, therefore be taken as a measure of the rate of total oxidation.

One of the objects of this investigation was to study the change in the nature of the water adsorption isotherm as the number of hydrophilic sites on the surface was increased. While in the preceding figure it would appear that the isotherm on the unoxidized surface was Type III and after 12 hours of oxidation

the isotherm was definitely Type II, this appearance is due
simply to the difference in magnitude. The two isotherms
are actually identical in shape up to the highest relative
pressures measured (0.5-0.6). Indeed, if the isotherms are
plotted in terms of $\theta(V/V_m)$ vs. $p/p_0$, all of the oxidized
samples as well as the unoxidized sample fall on a single
curve. The shape of the isotherm is therefore not influenced
by the fraction of the surface which is hydrophobic. If, as
has been postulated (1,2) the adsorption of water by Graphon
occurs by a clustering around hydrophilic sites, it would appear
that on the original sample these heterogeneities were not iso-
lated and randomly scattered about the surface but rather were
grouped together in patches perhaps at the edges of the graphitic
planes. Otherwise, it would be expected that increased adsorbate
interactions would show up in the isotherm as the distance between
hydrophilic sites decreased. Even with Sample A where 1/8 of the
surface was made hydrophilic and the maximum distance between
sites could be only approximately two molecular diameters, there
was no essential difference in the shape of the isotherm from
that of the unoxidized sample.

The weight change of Graphon on oxidation as observed
with Sample D is shown graphically on the next page. The figure
is very similar to the curves presented by Gulbransen and Andrew (8)

(8) E. A. Gulbransen and K. F. Andrew, Ind. Eng. Chem. 44, 1039 (1952).

for the oxidation of artificial graphite at 575°. Curve I repre-

WEIGHT CHANGE OF GRAPHON
ON OXIDATION

I  OBSERVED WT. LOSS

II  CALCULATED OXYGEN PICKUP

III  CORRECTED WT. LOSS
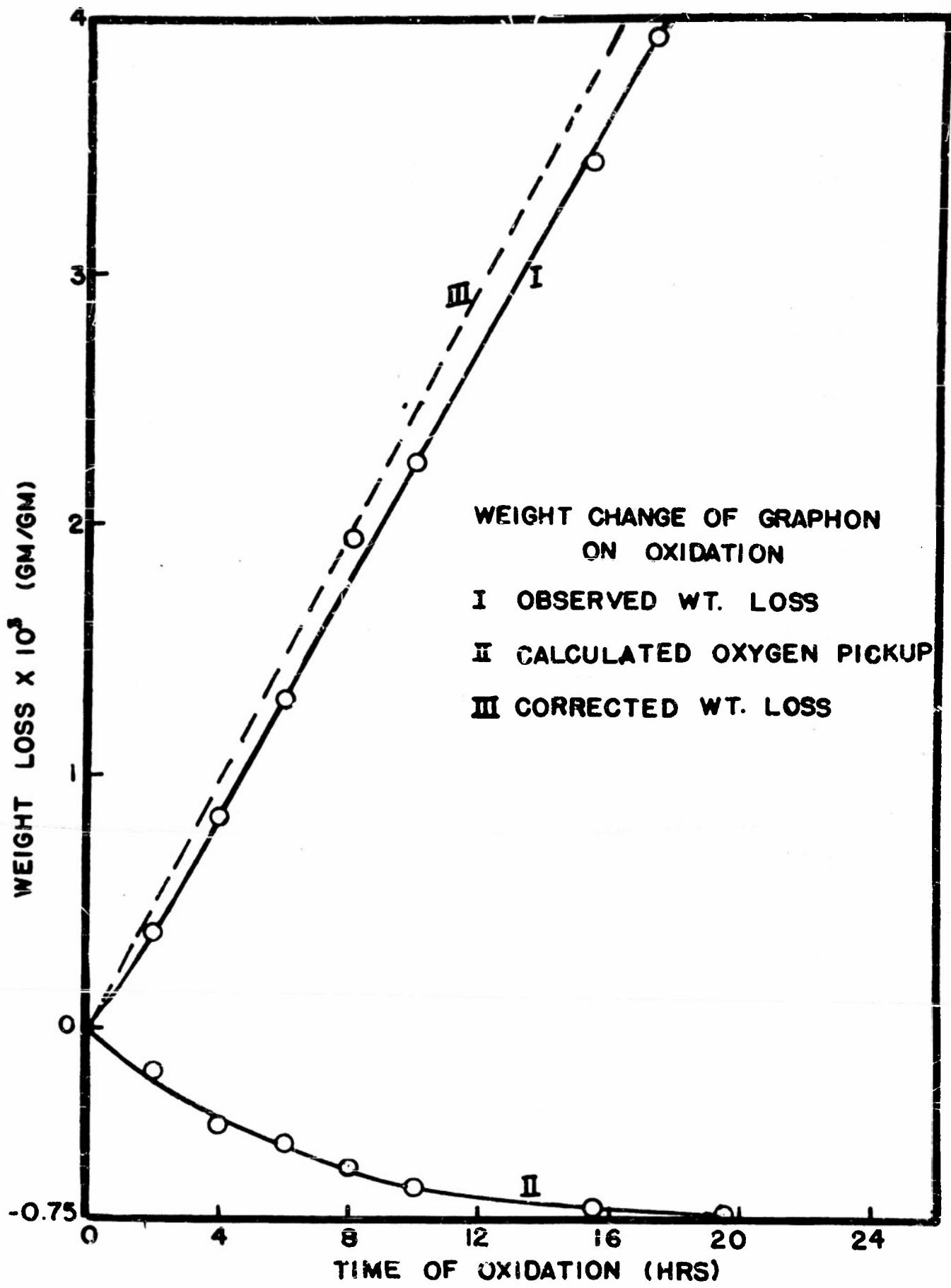
sents the observed loss in weight of the sample with increasing time of oxidation. Curve II is the calculated gain in sample weight due to the formation of surface oxide. This curve was calculated from the water adsorption $V_m$ values on the basis of one water molecule to each CO surface site. Curve III therefore represents the actual weight loss after correction for the gain in weight due to chemisorbed oxygen. The curves indicate that the rate of formation of volatile oxides is essentially constant over a period of twenty hours, but that the rate of stable surface oxide formation decreases with time.

Heats of immersion in water were measured for a number of the samples after the various treatments. Additional samples not shown in Tables I and II were also used in this study. These data are plotted in the next figure in ergs per cm.$^2$ of surface as measured by nitrogen adsorption against the fraction of the surface which was hydrophilic $\left(\dfrac{\Sigma H_2O}{\Sigma N_2}\right)$.

If the heat of wetting of the hydrophilic sites, $h_0$, and the hydrophobic carbon surface, $h_c$, remained constant with increasing amounts of surface oxide then a linear relation would be expected according to the equation:

$$h_I = \left(\frac{\Sigma H_2O}{\Sigma N_2}\right) h_0 + \left(1 - \frac{\Sigma H_2O}{\Sigma N_2}\right) h_c$$

where $h_I$ represents the observed heat of immersion. The best straight line drawn through the points would give $h_c = 31$ ergs/cm.$^2$

Figure plots HEAT OF IMMERSION (ERGS/CM²) on the vertical axis (ranging from -30 to -48) against $\frac{\Sigma H_2O}{\Sigma N_2} \times 10^3$ on the horizontal axis (ranging from 0 to 20).

Legend:
- ● UNOXIDIZED
- ○ OXIDIZED
- ◐ ACTIVATED
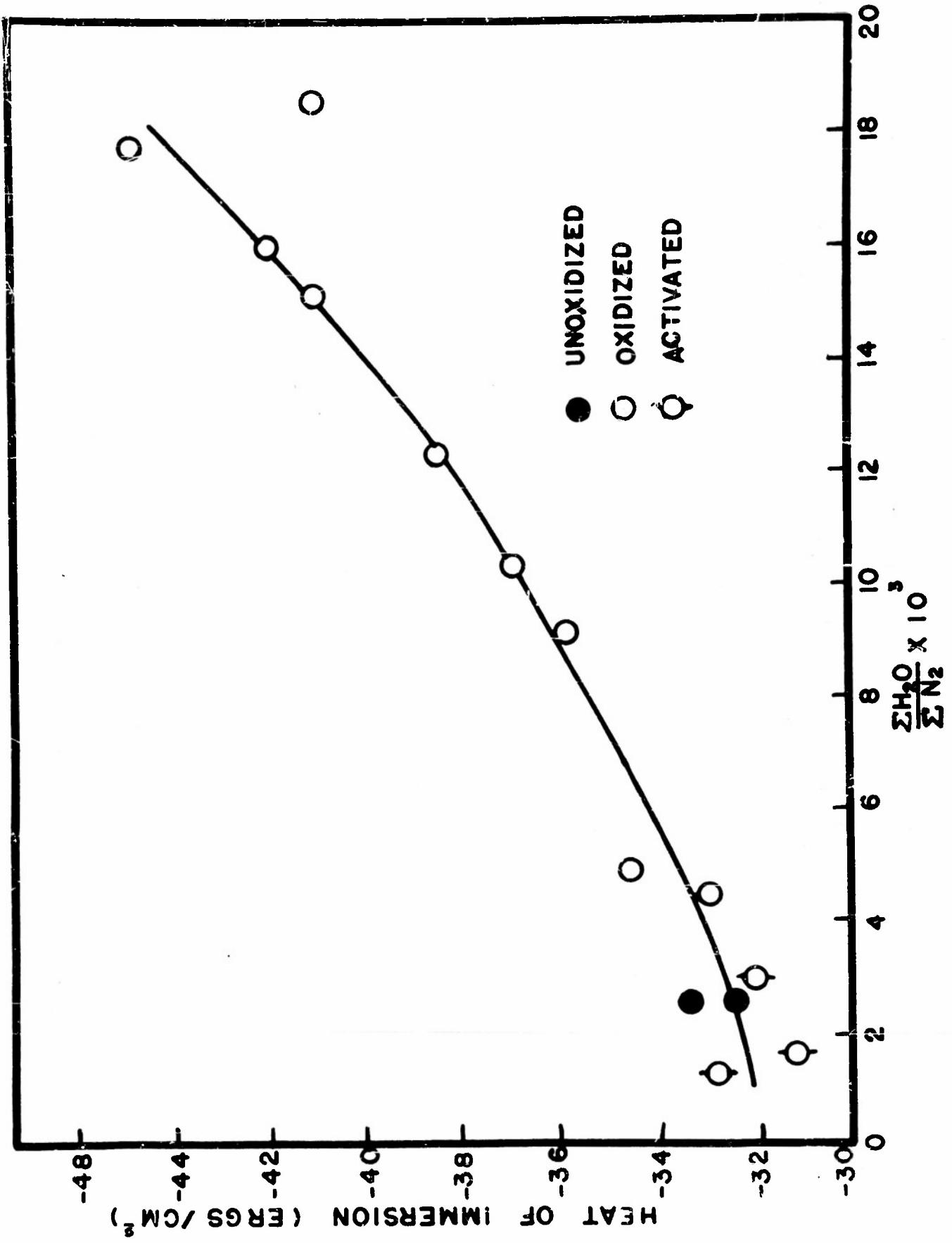
and $h_0 = 730$ ergs/cm.$^2$. The latter value is not unreasonable although somewhat higher than is usually obtained with hydrophilic surfaces. Since the $\theta$ experimental curve actually increases in slope it would appear that either $h_0$ increases or $h_c$ decreases or that both occur as the percentage of hydrophilic sites increases. A decrease in $h_c$ could be explained on the basis that the more energetic portions of the carbon surface would be most readily oxidized. However, water would interact with the carbon surface principally by non-polar van der Waals' forces and this interaction would be smallest on the carbon atoms (such as edge atoms) most readily oxidized. A more reasonable explanation is that $h_0$ increases due to increasing adsorbate interaction between neighboring patches of hydrophilic sites. This interaction would not show up in the isotherms except at relative pressures close to saturation.

# WORK NOW IN PROGRESS

A summary of current work undertaken in the period following that covered in the previous sections of this report is as follows:

1. As part of our study of the interaction of water with various types of surfaces, adsorption and heat of immersion measurements are being made with a bentonite clay. Thermodynamic calculations are to be made which should yield useful information concerning the surface properties of this material.

2. As a basis for the study of the inhibition of corrosion of metal surfaces, low temperature and room temperature oxidations of reduced nickel surfaces are being investigated by gas adsorption techniques.

3. A critical survey of the current data and theories of the role of various types of surface heterogeneities in corrosion has been prepared. The material will serve as a basis for a technical report to be submitted in the future.

4. Currently, a study of oxide-coated and reduced copper surfaces by physical and chemical adsorption techniques is being carried out. Further attention is to be directed to the nature of electronic defects in metals and in oxide films since this type of heterogeneity appears to influence strongly the oxidation process. Concurrently, the literature on organic corrosion inhibitors will be surveyed with the view toward studying treated metal samples by gas adsorption and calorimetric techniques.

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